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Flow chart of methanol in China

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ABSTRACT

Methanol is considered as one of the potential materials for fossil-based fuel since its available applications in the fields of fuel and chemical materials. China has become the biggest methanol production country since 2006, so analyzing the consumption, production and transportation of methanol in China has great importance. In the present paper, the flow chart of methanol from production to consumption in China has been systematically described. Chinese industry and statistics data are introduced to analyze and discuss the total and segmental methanol amount in both production and consumption. In China, most of the methanol is primarily consumed in the synthesis of formaldehyde, alternative fuels, and acetic acid synthesis with the corresponding percentage of 35%, 33%, and 8%. Synthesis approaches from methanol to these downstream products are analyzed and the variation tendencies of the demand on these downstream products are predicted. In 2011, about 22.27 million t methanol was generated on-site, in which, 63.7%, 23.0% and 11.3% are produced by coal, natural gas and coke-oven gas respectively. Energy flows of each synthesis process based on these feedstocks are given and the energy efficiency are calculated and compared. As for the transportation, approximately 82.6% of methanol is relied on overland freight, 9% by marine and the rest 8.4% by train.

Contents

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1. Introduction

The modern era is in urgent need of alternative energies for its sustainable development under the serious threatening of fossil-based materials' depletion [1–5]. Nuclear energy, wind energy, solar energy, hydro-energy, bio-energy, hydrogen energy, and the transformed electrical energy are considered promising alternative energies in the future, but the fossil-based materials will not completely quit the stage of history since they are the utmost important raw materials in various chemical industries. As well-known, methanol is a promising alternative fuel especially for transportation field [6,7]. Meanwhile, it is an utmost important raw materials in chemical industries. Therefore, making investigations on the production and application of methanol have attracted more and more scientists since its available applications in the fields of fuel and chemical materials, and making plans and projects on the production and application of methanol have attracted more and more authorities[8–10].

In China, the methanol energy industry is established at the medium-20 century, and the production capacity on methanol is increasing in a vibrating tendency and has been increased by approximately 16 times during the past 16 years (from 1995 to 2011) (as shown in Fig. 1) [11]. Over the same period, the mean increase extent on the production capacity of methanol throughout the whole world is just triple. Fig. 2 shows the corresponding production capacity increment in China and the world. From the beginning of 2002, China's methanol industry strode into a fast development period and the annual increment outclass the worldwide level from then on. Thus, the development of China's methanol energy industry can be considered as a typical example in both production capacity scale and production capacity increment. Due to its fast increment, China's sharing ratio on the annual production capacity of methanol is continuously enlarged. Since the year 2006 at which China firstly becomes the biggest production country with 13.95 million t per year, the sharing ratio is consistently increasing. At 2010, it is even beyond half the global total production capacity.

Although China has its own large production capacity, 10% of the methanol consumed in China is imported. The import volume of methanol increased 14.2% annually, from 1.52 million t (year 2001) to 5.73 million t (year 2011) [11]. A dozen of countries benefit from this and export their methanol to China, such as Saudi Arabia, Malaysia, Qatar, Bahrain, Indonesia, New Zealand, India and Brunei [11].

Thereby, China's methanol industry is too big to ignore, reviewing and analyzing the flow chart (through production to consumption) of methanol in China can not only provide further information on the understanding of China's present and future methanol industry, but also provide significant information to the main methanol exporters. The flow chart reported in the present paper can give some valuable suggestions to the countries those will to and/or begin to establish their national methanol industry based on China's experiences.

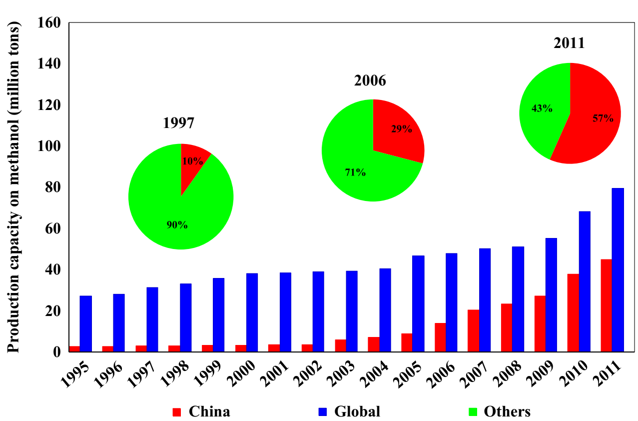

Fig. 1. Comparison of production capacity on methanol between China and the global.

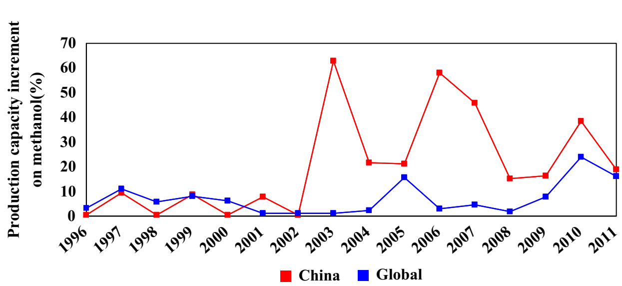

Fig. 2. Comparison of production capacity increment on methanol between China and the global.

2. Flow chart of methanol in consumption

In China, most of the methanol produced from fossil fuels and coke-oven gas is consumed primarily in the manufacturing of formaldehyde, alternative fuels, and acetic acid synthesis, which are utmost important materials for the development of modern construction industry, modern transportation industry, and modern chemical industry. Since the end of 1970s, the development of China's modernization was accelerated, this resulted in a skyrocketing demand of methanol. During the past three decades, the annual methanol consumption has increased by 71 times from 0.33 million t at 1983 to 23.84 million t at 2011 [12]. It can be unambiguously predicated that the annual methanol consumption in China will continuously increases in a long-term for the further developments of modernization.

2.1. Methanol consumption in formaldehyde synthesis

Formaldehyde synthesis is the major aspect to the methanol consumption for China, and occupies approximately 35% of the annual total methanol consumption, as shown in Fig. 3. Nowadays, China's industrial formaldehyde production from methanol is mainly based upon three approaches: (i) Dehydrogenation of Methanol (DoM) approach; (ii) Oxidation of Methanol (OoM) approach; and (iii) Oxidative Dehydrogenation of Methanol (ODoM) approach.

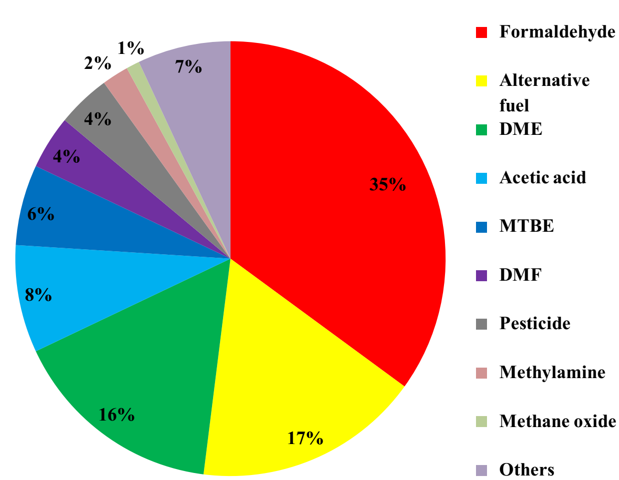

Fig. 3. Sharing ratio of each aspect on the consumption of methanol in China.

Table 1
Reaction pathway of methanol to formaldehyde on three approaches.

Approaches	Equation	Temperature (K)	Transition efficiency (%)	Selectivity (%)
DoM approach	$CH_3OH \rightarrow CH_2O + H_2$	670–970	45–70	75–86
OoM approach	$CH_3OH + 1/2O_2 \rightarrow CH_2O + H_2O$	540–623	99	91–94
ODoM approach	$CH_3OH \rightarrow CH_2O + H_2$ $CH_3OH + 1/2O_2 \rightarrow CH_2O + H_2O$	520–620	> 90	85–95

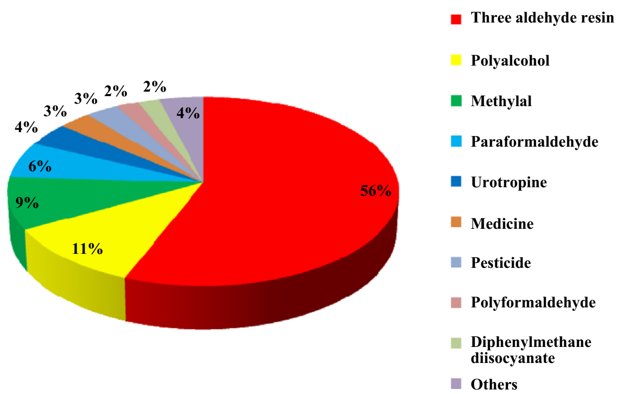

Fig. 4. Sharing ratio of each aspect on the consumption of formaldehyde in China.

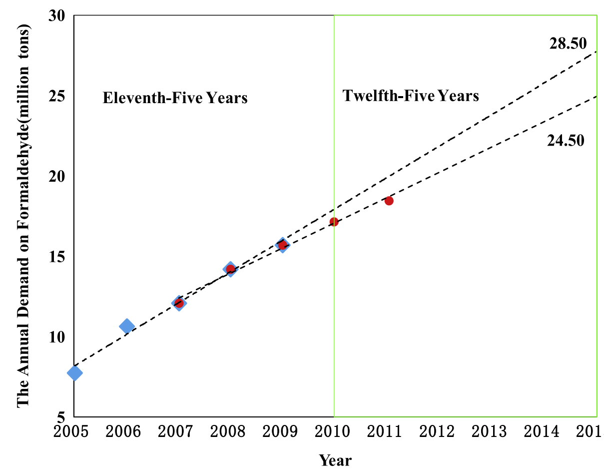

Fig. 5. Variation tendency of the annual demand on formaldehyde.

Among the three approaches, DoM approach is the only approach to the production of anhydrous formaldehyde. In addition, DoM approach can high-fidelity control the detailed reactant steps by adopting and adjust the catalyst since it can employs various kinds of catalysts (such as metal catalyst [13–15], metal oxide catalyst [16–18], carbonate catalyst [19–21], Molecular sieve catalyst [22–24], etc.). However, this approach has not been widely applied, especially in bulk, due to the complex control strategies. Albeit OoM and ODoM approaches can hardly produce anhydrous formaldehyde, and they are the two commonly employed approaches in the practical production of formaldehyde (at least in China) due to the higher transition efficiency, the higher purity of produced formaldehyde, and the simpler the reactant steps, as listed in Table 1 [25]. The main difference between the later two approaches is the equivalence ratio of the methanol-air mixtures they employed. OoM approach employs lean mixtures (in which the volume fraction of methanol is less than 6.7%, namely under the low band of the explosion limit) as the reactants, while ODoM approach employs rich methanol–air mixtures (in which the volume fraction of methanol is larger than 36.5%, namely above the upper band of the explosion limit) as the reactants.

Fig. 4 shows the sharing ratios of each aspect on the consumption of formaldehyde in China. As can be seen, the produced formaldehyde is mainly employed to the manufacturing of three aldehyde resin, polyalcohol, methylal, paraformaldehyde, urotropine, medicine, pesticide, polyformaldehyde, diphenylmethane diisocyanate [26–28], etc.

As the deeply development of China's modernization, the demand on formaldehyde, which is one utmost important materials in the construction, is rapidly increased. At the year of 2011 (beginning of the 12th-Five Years), the annual demand of formaldehyde had reached 18.48 million t, which is approximately 2.4 times to the amount at 2005 (beginning of the 10th-Five Years) [12]. According to the variation tendency of annual demand, it can be predicated that the annual demand at 2015 will reach 24.50–28.50 million t which is approximately 1.2–1.5 times to the amount at 2011, as shown in Fig. 5. If all the produced formaldehyde is obtained by OoM and/or ODoM approach, 8.56–9.45 million t methanol will be consumed at 2011 and 13.26–14.65 million t will be consumed at 2015(considering the concentration of formaldehyde production is 40% by mass). If all the produced formaldehyde is obtained by DoM approach, 17.46–22.28 million t methanol will be consumed in 2015.

2.2. Methanol consumption relevant to vehicle fuels

China's vehicle industry rapidly develops in the past 20 decades, the vehicle population is skyrocketing increased, and the demands on vehicle fuels are correspondingly increased. In China, most commercial vehicles are still employ gasoline as the fuel, and Methyl Tertiary Butyl Ether (MTBE, a main production derived from methanol) is one utmost important additive for the gasoline [29]. Thereby, it can be predicated that, the demanding of MTBE as the additive for gasoline fuel will be increased. Furthermore, the research and the development of alternative fuels fueled vehicles have become hot topics in China's vehicle industry, so more and more vehicles will employ alternative fuels instead of gasoline in the future. The demanding on methanol will not be reduced since both the methanol itself and Dimethyl Ether (DME, another main production derived from methanol) are promising alternative fuels.

2.2.1. Methanol consumption in MTBE synthesis

Methyl Tertiary Butyl Ether (MTBE), a volatile, flammable, and colorless liquid, is a gasoline additive which can be employed as an oxygenate to raise the octane number. Adding MTBE is an ordinary and profitable approach to improving the quality of the catalytic cracking gasoline which occupies approximately 40% of the total gasoline in China, and thus the demands on MTBE is great in China due to the increasing consumption on gasoline [30,31]. Fig. 6 shows the formulation of #93 gasoline in Yangtze River Delta and Bohai Rim in China. As can be seen, in the formulation of #93 gasoline, the mass fraction of #90 gasoline is 40–50%, while the mass fraction of MTBE is 8–10% [32]. In addition, the commercial price of #90 gasoline is approximately 1450 US dollar per ton,

while the commercial price of MTBE is approximately 1350 US dollar per ton. Thereby, properly increasing the mass fraction of MTBE in the formulation of #93 gasoline can noticeably decreasing the cost of #93 gasoline associated with the enhancement on the general quality.

In China, the production of MTBE is mainly based on the etherification of methanol and isobutene along with catalyst (such as mineral acid [33,34], cation exchange resin [35,36], molecular sieve based catalysts [37,38]). The etherification reaction can be accurately controlled based upon the Markovnikoff's Rule to produce Methyl Tertiary Butyl Ether rather than Methyl Isobutyl Ether. The transition efficiency can reach to 75–90%, and the accurate efficiency can be adjusted by employing different kinds of catalyst and/or controlling the reaction temperature [39].

As an essential material of the commercial gasoline, the annual demand of MTBE is increased with the increase in gasoline fuel. During the last decade, China's annual demand on MTBE is correspondingly increased by triple times (from 1.16 million t at 2003 to 3.56 million t at 2011) accompanied with the increase of vehicle population. As can be seen in Fig. 7 [12], until the end of 11th-Five Years (the year of 2010), the rise in annual demand on MTBE is relative stable in approximately a linear tendency. However, from the year of 2010, the annual demand on MTBE is steeply increased in a huge step, which is mainly attributed to the increase of blending proportion to the gasoline. Based upon the current rise tendency, it can be predicted that the annual demand on MTBE at the end of 12th-Five Years (namely, the year of 2015) will reach 3.90–5.80 million t with an average annual growth rate of 2–12%. According to the current transition efficiency of methanol to MTBE, the annual demand of methanol will reach 1.62–2.88 million t. Albeit the fraction of MTBE within gasoline will be continuously reduced due to the appeals on environmental protection, the annual demand on MTBE won't be significantly reduced due to the present huge cardinal number of gasoline.

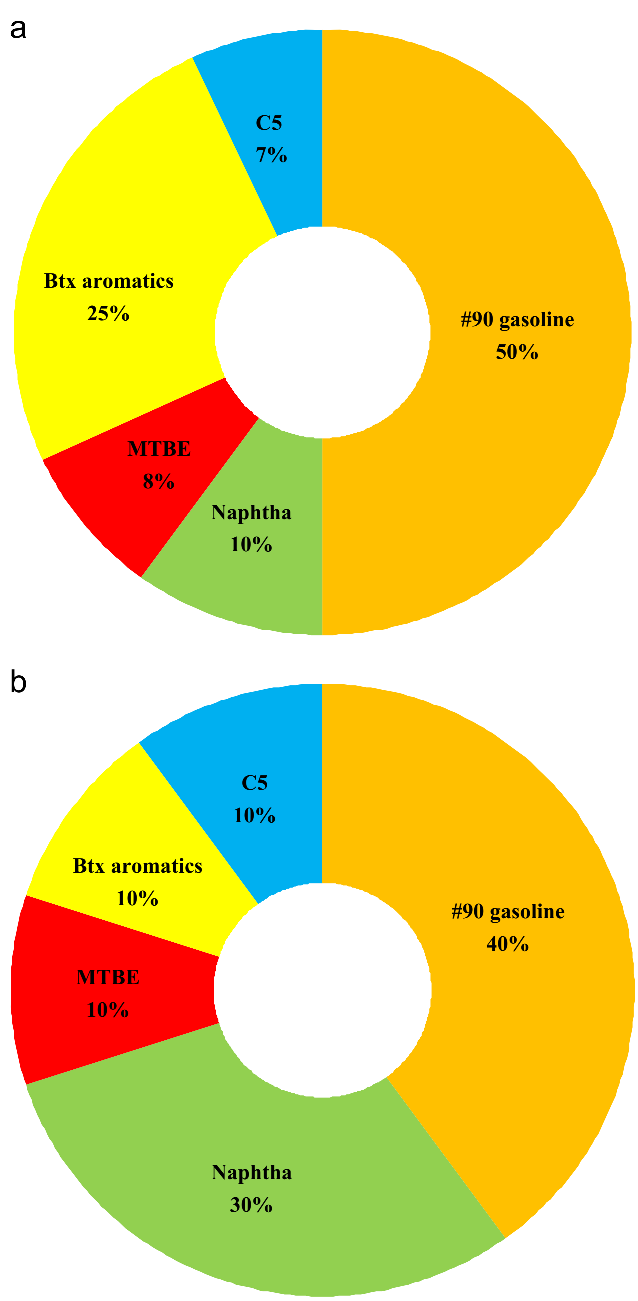

Fig. 6. (a) Formulation of commercial gasoline (#93) in China: in Yangtze River Delta. (b) Formulation of commercial gasoline (#93) in China: in Bohai Rim.

2.2.2. Methanol consumption in DME synthesis

Dimethyl Ether (DME), the simplest ether, is widely considered as one promising alternative fuel in diesel engines, spark-ignited engines (30% DME with 70% LPG), and gas turbines owing to its high hexadecane number (approximately 105–138% of that of diesel). A diesel engine fueled with DME can obtain higher thermal efficiency (at least 2–3%) associated with lower nitrogen oxides (approximately 30%), lower carbon monoxide (approximately 40%), lower unburned hydrocarbon (approximately 50%), and soot-free. Thus DME as the alternative fuel in diesel engines is widely employed in many countries to meet the stringent emission regulations (such as EURO 5, US 2010, 2009 Japan, etc.). Besides that, DME is also widely employed as civil LPG alternatives due to the safer in storage-to-transportation process and the higher in combustion efficiency. In China, DME is primarily produced by the dehydration of methanol in the presence of a different catalyst (such as silica–alumina) with a higher transition efficiency (up to 86%) [40].

China's annual demand on DME is increased with the development of alternative fueled vehicle as well and the popularization of civil LPG. As shown in Fig. 8, the annual consumption of DME is stably increased (with a mean annual growth rate of 30%) during the periods of 11th-Five Years [12], and is steeply increased (the annual growth rate is approximately 40%) at the beginning of 12th-Five Years due to the national policies on the application of DME in vehicle and civil LPG. It can be predicted that, the annual

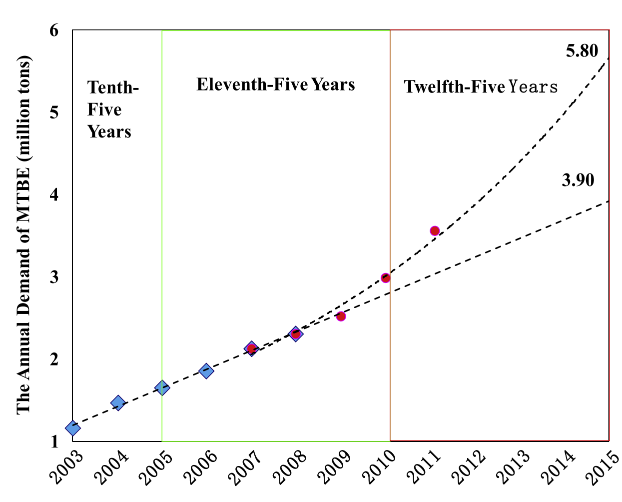

Fig. 7. Variation tendency of the annual demand on MTBE.

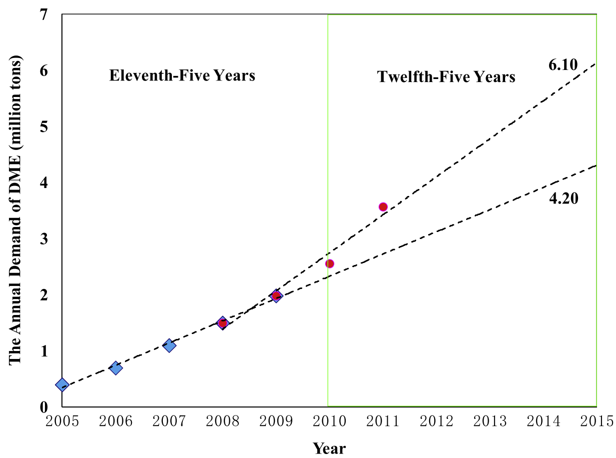

Fig. 8. Variation tendency of the annual demand on DME.

demand on DME will continuously increase with the further development of DME fueled vehicles and the promotion of civil DME. Based upon the current rise rate, the annual demand of DME will reach 4.20–6.10 million t at the end of 12th-Five Years, which will consume 6.40–9.20 million t methanol.

2.2.3. Methanol consumption as an alternative fuel

Besides employed to produce MTBE and DME, methanol can be directly employed on a limited basis to fuel internal combustion engines. Due to its preeminent advantages in high octane number and high oxygen content, a vehicle fueled with methanol can afford higher compression ratio, obtain higher thermal efficiency, and emit lower emissions[41–43], thereby pure methanol has been required by rule to be employed in various heavy-duty cars and trucks since the late 1940s. Albeit the value of methanol's lower calorie value only approximately half of gasoline/diesel (19.678 MJ/kg for methanol and 40 MJ/kg for gasoline/diesel), The brake specific methanol consumption just increase 50% consumption compared with gasoline and/or diesel owing to the higher thermal efficiency.

In China, methanol fuels employed in practical applications are mainly three modes: M100 (pure methanol), M85 (the mass fraction of methanol is 85%), and M15 (the mass fraction of methanol is 85%) [44]. Employing M100 as spark-ignited engine fuel can significantly improve the thermal efficiency due to the higher compression ratio (up to 19.5), but M100 hardly can be promoted in bulks due to its fierce toxic property. Compared with M100, taking M85 as the fuel can noticeably reduce the general level of the toxicity associated with the similar engine's performances and the employing of corrosion-resistant materials for critical parts of the pipeline system is needed. Compared with the above two, M15 has the lowest general level of the toxicity, but the vehicle dynamic performances can be slightly improved due to higher compression ratio and the changes for the injection and combustion system are unnecessary.

At the beginning of 2011, Ministry of Industry and Information Technology of the People's Republic of China starts the Program (2011–2013) on the Application of M85 and M100 in spark-ignited engines, and takes Shanghai City, Shaanxi Province and Shanxi Province as the pilots. Under the Program, the annual consumption on methanol as vehicle fuel in 2011 is approximately 2.30 million t, which saves approximately 1.05–1.24 million t gasoline. It can be confirmed that, the annual demand on methanol as vehicle fuel will continuously increases under the further development of alternative fuels fueled vehicles in China.

2.3. Methanol consumption in acetic acid synthesis

Acetic acid, a colorless liquid, is the main component of vinegar [45] (apart from water, vinegar is roughly 8% acetic acid by volume), and has a distinctive sour taste and pungent smell. Besides the production of vinegar, acetic acid is mainly employed as an utmost important raw material in chemical industries, such in the synthesis of vinyl acetate, acetate, and ethyl chloroacetate, etc. [46].

The acetic acid can be obtained from methanol by two approaches: (i) carbonylation of methanol at higher pressure (CoMH); (ii) carbonylation of methanol at lower pressure (CoML). By the CoMH approach, acetic acid is produced via carbonylation of methanol and carbon monoxide in the aqueous acetic acid solution under a higher pressure (up to 70 MPa) and higher temperature (500–530 K), and cobaltcarbonyl is employed as the catalyst and iodomethane is employed as promoter. By the CoML approach, acetic acid is also synthesized by carbonylation of methanol and carbon monoxide, however the recanting pressure is just about 3 MPa due to the different catalyst, rhodium triiodide [47,48]. Table 2 shows the comparison on the feedstock consumption and energy consumption in both approaches. As can be seen, adopting the CoML approach can not only significantly save both the consumption of methanol and carbon monoxide, but also save the energy consumption during the production process. Therefore, the CoML approach is mainly employed in the modern chemical industries.

In China, the consumption of acetic acid fast increases with the rapid development of fiber, coating, adhesive industry, and the annual consumption have been increased by 22.1% during the 11th-Five Years (namely, 2005–2010) as shown in Fig. 9. In the recent two years, the increase of China's real estate industry has slowdown duo to the transaction limit from the government, so the growth rate of the acetic acid demand declined to 18.9% with the decreasing acetic acid coating and adhesive consumption [12]. It can be predicted that

Table 2
The consumption for producing per ton acetic acid.

Items	CoMH approach	CoML approach
Methanol (t)	0.61	0.56
Carbon monoxide (t)	0.78	0.54
Water consumption (t)	1.85	1.56
Vapor consumption (t)	2.75	2.20
Power consumption (kW h)	350	29

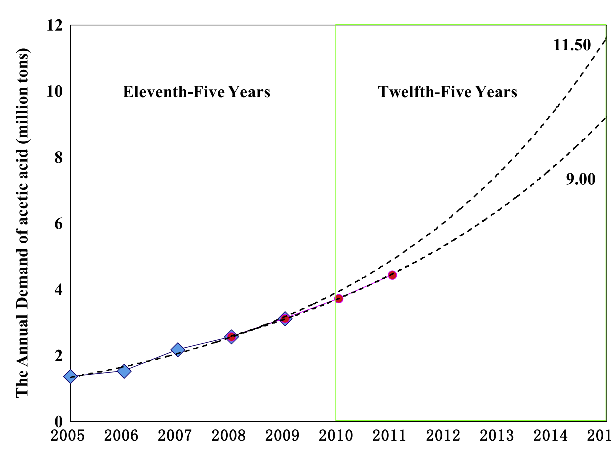

Fig. 9. Variation tendency of the annual demand on acetic acid.

in the next five years, the increase tendency will not change too much and Chinese annual demand of acetic acid will reach 9.00–11.50 million t by the year 2015. The methanol consumption will be 5.49–7.02 million t by the CoMH approach and 5.04–6.44 million t by the CoML approach accordingly.

3. Flow chart of methanol in production

Nowadays, methanol is mainly produced based on the catalytic hydrogenation of carbon monoxide and carbon dioxide [49–51], and the classical progress includes the preparation of syngas, the purification of syngas, the synthesis of methanol, the rectification of crude methanol. Moreover, there are other alternative emerging approaches, such as carbonization of wood [52,53], pyrolysis of biomass [54–56], extracting of oil [57], oxidation of methane [58], ammonia-oxidizing bacteria [59] and so on. However, most of them are still employed in medium- and even small-scales due to low covert efficiency, immature technologies, worse environmental affects, and other weaknesses at current stage [52–59].

Considering the purity and production process, natural gas oxidation is commonly regarded as the utmost promising approach to the batch production on methanol syngas and has been excessively employed in many countries (such as Chile, Canada, Iran, Saudi Arabia, etc.) [9,10]. Although some scholars believe biomass-based approach will be the utmost promising approach to methanol in the future [60], most countries still take coal, natural gas and coke-oven gas as the major sources in the current and a medium-long term even a long-term.

3.1. Methanol produced from coal

Methanol syngas production from coal is mainly based on the intermittent gasification process in the fixed-bed [61,62]. The primary syngas from the fixed-bed has a lower ratio of hydrogen to carbon, which hardly be employed to produce methanol. Thus, prior to the synthesis process, it should be made excessive carbon monoxide and water transformed to sufficient hydrogen gas for increasing the ratio of hydrogen to carbon to an ideal level.

Since coal is rich in carbon, hydrogen, oxygen, nitrogen, sulfur and other inorganic substance, the purity of the coal-based methanol syngas is related lower; meanwhile, the purification process is much complicated due to the various by-products. However, the coal-based syngas can employ various gasifying agents, such as oxygen gas, water vapor, hydrogen gas, and others [63]; thus, the production of methanol based upon coal has been favored in the past decades, especially for the low-purity methanol demands.

Fig. 10 shows the energy flow in the process of coal-based methanol synthesis [61,62]. As for the primary, stuff, the consumption amount of coal for producing per ton methanol is about 1.5 t with 51 GJ energy carried. The energy contained in other feedstocks is 0.120 GJ for fresh water, 0.370 GJ for desalted water and 0.075 GJ for fresh air respectively. Electric energy flow in the whole process is 8.761 GJ, and the abandon gas generated with methanol is 400 m^3 with 3.808 GJ energy carried. Considering the low calorific value of methanol is 19.93 GJ/t and the high calorific value is 22.70 GJ/t, the energy efficiency of coal-based methanol synthesis is among the range of 35.3–40.1%.

According to the production approach to methanol, it can be found that hydrogen gas and carbon monoxide are the main compounds of the syngas. Actually, hydrogen gas and carbon monoxide are by-products during the production of ammonia [64], thus the co-production of ammonia and methanol (mainly synthesized by hydrogen gas and carbon monoxide) has been considered, researched, and employed by China in the past decades.

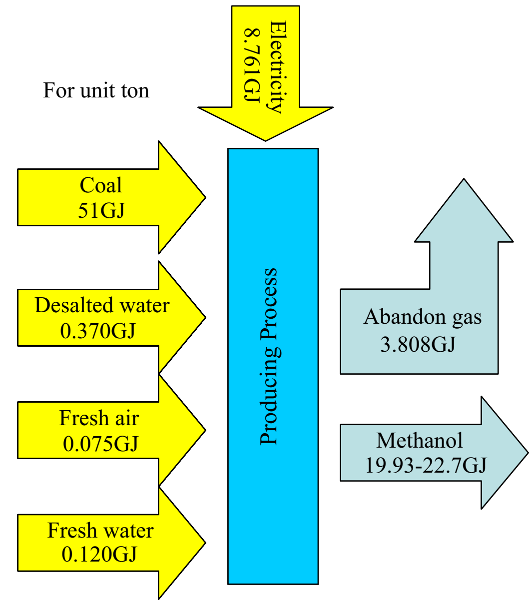

Fig. 10. Energy flow in the process of coal-based methanol synthesis.

The methanol synthesis adopting by-products (mainly hydrogen gas and carbon monoxide) during the production of ammonia is realized by the introducing of copper-based catalysts, at pressure 5–15 MPa. The by-products (hydrogen gas and carbon monoxide) can be fully used with no waste in the process of methanol synthesis. As calculated, the methanol yield is about 150 kg/t ammonia in the co-production process [65]. In China, the recent production of ammonia is mainly depended upon coal, thus taking coal as the feedstock to the co-production of ammonia/methanol is the utmost promising solution. The annual production of methanol by co-production approach is about 3.86 million t in the year of 2006, and is about 8.78 million t in the year of 2011 with an annual average growing rate of approximately 17.8%. In fact, the coal-based methanol is the main source of China's commercial methanol (as shown in Fig. 11), the sharing ratio of the annual total production has been increased 4.3 folders in the past five years from 40.2% at 2006 to 63.7% at 2011 [66].

Compared to other possible and potential feedstock, the reserve of coal is sufficient in China. According to British Petroleum statistical report, China's proven coal reserve is 114,500 million t at the end of 2011, approximately 13.3% of the total world; and the annual production amount continuously increases to 2569 million t with an average annual growth rate of 9.7%. Thus, adopting coal as the feedstock will be an utmost important approach to commercial methanol in a long-term for China. Besides that, the cheap coal price still make the coal-based methanol has a competitive price. When the coal price is 96.6 US dollar per ton, the produce cost for per ton methanol is about 320.3 US dollar.

3.2. Methanol produced from natural gas

The methanol syngas derived from natural gas is mainly based on steam-reforming and/or oxidation of methane [67,68]. In China, the preparation of syngas is mainly realized by two steps. Firstly, about a quarter of methane has been transformed to carbon monoxide or carbon dioxide via steam-reforming. Then, for the remaining three-quarter methane, the produced carbon monoxide or carbon dioxide, and hydrogen have been partially oxidized in binary furnace to efficiently produce syngas. After that the

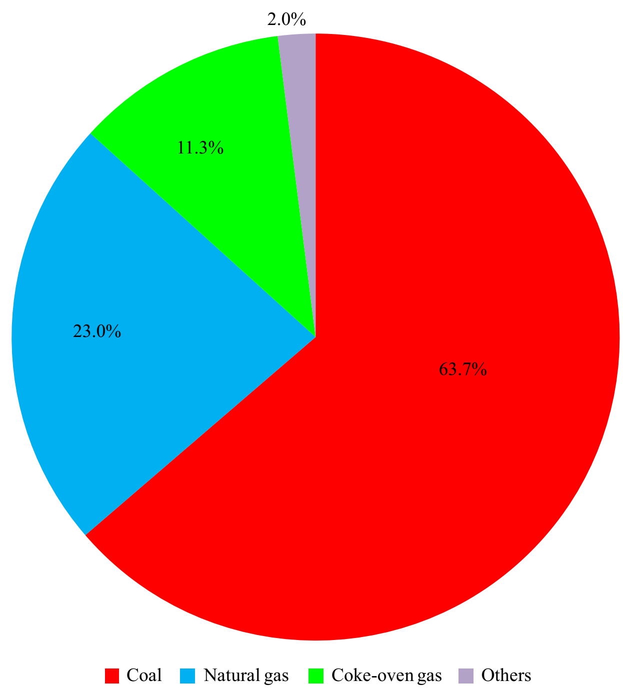

Fig. 11. Sharing ratio of each aspect on the production of methanol in China.

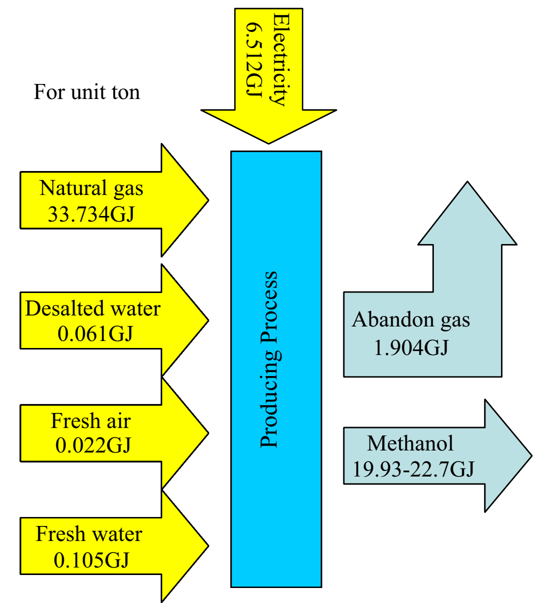

Fig. 12. Energy flow in the process of natural gas-based methanol synthesis.

prepared syngas would be transformed to methanol ultimately after a serious of process, and the detailed process can be found in Ref. [69].

Natural gas-based approaches have preeminent advantages in high-purity and simply process. Natural gas, a kind of compound matters including 80–90% methane and other alkane, can be easily transformed to carbon monoxide, carbon dioxide and hydrogen with few impurities, so the synthesis process to methane based upon natural gas is the sufficiently simpler than that based upon coal. Furthermore, different to the huge amount of water demanded by coal-based methanol, the synthesis of natural gas-based methanol just employ limited amount of water.

Fig. 12 shows the energy flow in the process of natural gas-based methanol synthesis [69]. The 6.512 GJ energy from electricity powered the whole process. Energy contained in the main feedstock–natural gas is 33.734 GJ, contained in the other feedstock (desalted water, fresh air and fresh water) is 0.189 GJ totally. 1.904 GJ energy is taken away by the abandon gas. So the energy efficiency of natural gas-based methanol synthesis is among the range of 51.7–58.9%.

In China, the natural gas industry has skyrocketed in the past decades, and the application of natural gas in the production of methanol has been correspondingly increased. In the year of 2011, the annual production amount of natural gas-based methanol increased to 5.12 million t, approximately 23.0% of the annual total production. However, the tendency on sharing ratio of total methanol production seems to be stopped even reversed in a predicated term due to the depleting natural gas reserve and the enlarging natural gas consumption. According to the statistic overview reported by British Petroleum, China's proven natural gas reserve is just 3.1 trillion N m^3, and the ratio of reserve to production is just 29.8 years [70]. In fact, the demand of natural gas in China has increased straightly with the economic development and it is mainly consumed for ammonia chemical fertilizer and civil LPG, so there is little allowable natural gas to be applied for the production of methanol.

Based on the above discussions, it can be easily concluded that reducing and limiting scale of natural gas-based approaches on methanol production is an inevitable tendency for China, and the sharing ratio of natural gas-based methanol must be corresponding reduced.

Nevertheless, the natural gas-based approaches won't be completely abandoned in China. The gas-based methanol is widely used in some fields as pharmacy and vehicle fuel. Furthermore, China's unbalance energy structure makes some local regions and/or provinces (such as Qinghai, Sichuan) owned rich natural gas reserve but few other available energy sources; and the natural gas-based methanol can provide necessary energy demand in certain levels. And the related technologies about the natural gas-based approaches (especially the technologies on the enhancement of transition efficiency) will be further developed for the sustainable development.

3.3. Methanol produced from coke-oven gas

Coke-oven gas is a by-product during the process of coking. Since it is mainly composed of hydrogen (55–69%) and methane (23–27%), it can be employed to produce methanol after simple processing [71].

The key steps of the coke-oven gas-based production process are the transformation and desulfuration of syngas, the following process including compressing and synthetizing is similar with the natural gas-based approaches [72]. As well known, the ingredient of coking differs greatly due to the different kinds of source-coal; and the raw coke-oven gas has a neglected content of sulfur which can cause poisoning of the catalyst, so the pretreatment process is indispensable and relatively complex. It includes the process of cooling/condensation (at 295–298 K), compression (at 25 kPa), tar gathering and removing (tar concentration less than 0.05 g/m^3), desulfuration (concentration of sulfur dioxide with the range of 0.02–0.3 g/m^3), deamination, debenzolization (benzene concentration with the range of 0.2–0.4%) and naphthalene removing (naphthalene concentration less than 0.05 g/m^3) [73].

The methanol synthetizing based coke-oven gas can be accomplished in two different approaches: (i) non-catalytic partial oxidation (NCPO); (ii) catalytic partial oxidation (CPO). In NCPO approach, the catalytic can be omitted and the pretreatment process of syngas can be simpler. In CPO approach, the coke-oven gas and oxygen consumption are lower than that of non-catalytic partial oxidation approach and there is no production of

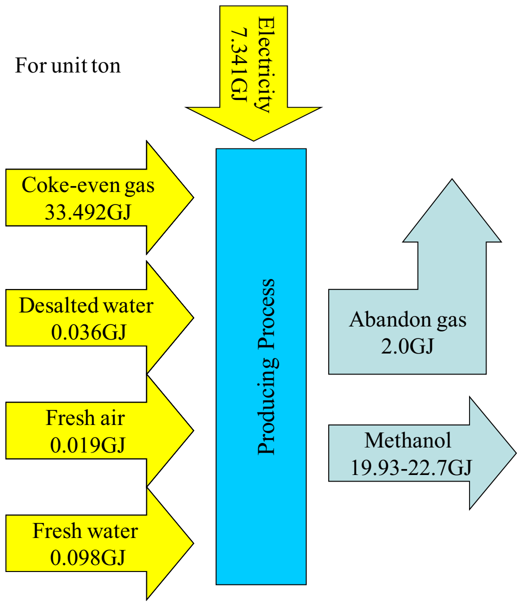

Fig. 13. Energy flow in the process of coke-oven gas-based methanol synthesis.

soot in the process. Totally, the cost of catalytic partial oxidation for per ton of methanol is 80–87% of that of non-catalytic approach.

Fig. 13 shows the energy flow in the process of coke-oven gas-based methanol synthesis [74]. The consumption amount for producing per ton methanol is about 2000 N m^3 with 33.492 GJ energy carried. Correspondingly, for providing oxygen to oxide the carbon monoxide and carbon dioxide transformed from coke-oven gas, it needs 20 N m^3 fresh air, with 0.019 GJ energy carried. The energy contained in the desalted water is about 0.036 GJ while 0.098 GJ in the fresh water, and the electric energy expended in the whole process is 7.341 GJ. Barring the abandon gas energy of 2.0 GJ, the energy efficiency of coke-oven gas-based methanol synthesis is among the range of 51.1–58.2%. Above all, the energy efficiencies of coke-oven gas-based and natural gas-based methanol synthesis are almost the same, the energy efficiency of coal-based methanol synthesis is lower.

Nowadays, the synthesizing technology has developed very fast in China, and it has contributed more than 10% of the national methanol production capacity (as shown in Fig. 11). In 2011, the coke yield was about 300 million t, it can bring 129 billion N m^3 of coke-oven gas (considering the convert efficiency: 430 N m^3 coke-oven gas vs. 1 t coke) [75]. Among this, about 90 billion N m^3 can be recycled used for heating on the product line and synthesizing other chemical productions, but there still 30 billion N m^3 left obsoleted which can be employed to the production of methanol.

4. Transportation of methanol in China

In China, most of provinces and cities (besides Beijing, Tibet, Hong Kong, Macao and Taiwan) can produce methanol, but the consumption of methanol is always not on-site. The issue is mainly attributed to the difference in the base of industrial development and the mode of economic development.

For resolving the issue, making the improvement of the productivity concentration and the optimization of the industrial layout are utmost important, but the improvement and the optimization will not be accomplished overnight. Therefore, making transportation of methanol is the utmost effective solution to the unbalance between the on-site production and the not-on-site consumption in most China's provinces.

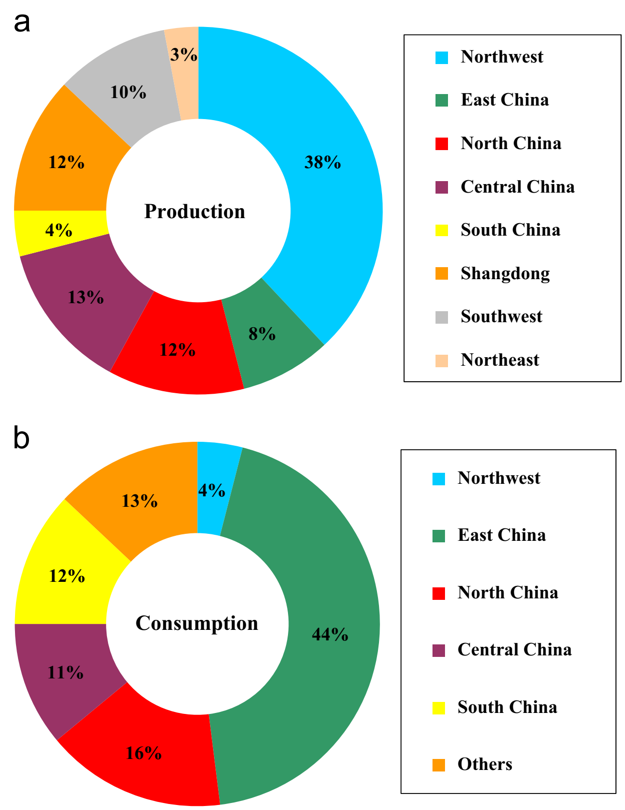

Fig. 14. (a) Sharing ratio of regions on the production and consumption of methanol in China: production regions. (b) Sharing ratio of regions on the production and consumption of methanol in China: consumption regions.

Fig. 14 illustrates the Sharing ratio of regions on the production and consumption of methanol in China. As shown, 38% of the China's methanol is produced in Northwest, but only 4% is consumed on-site. Correspondingly, in East China, the methanol production occupies 8% of the gross but the consumption scale here is 44% [76], which means large amount of methanol need to be transported across China. In the current China, approximately 82.6% of methanol is relied on overland freight, 9% by marine in which most is imported, and the rest 8.4% by train. For the transportation overland freight, there exists several issues, such as expensive cost, high insecure, etc. Thus it should change the traditional transportation project for improving the efficiently transport capacity between the methanol production and consumption regions

5. Conclusion and discussion

Since the Industrial Revolution, fossil-based materials, such as coal, petroleum, natural gas are widely employed in the fields of energy industries and chemical industries as the energy source and the raw materials. As the demands on energy increasing, the traditional primary fossil-based fuels have to be prepared for being replaced by those utmost promising alternative energies, such as nuclear energy, wind energy, solar energy, hydro energy and the transformed electrical energy. However, those promising energies hardly be employed to replace the fossil-based materials as the raw materials in the chemical industries. Compared to the traditional primary fossil-based fuels and those promising alternative energies, methanol is an utmost important alternative energy and materials for both the energy industries and the chemical industries.

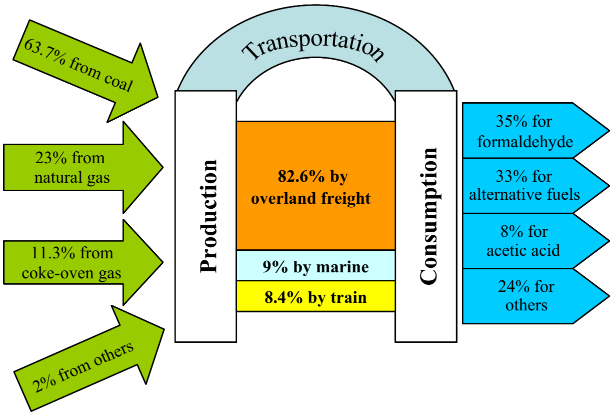

Fig. 15. Total flow chart of methanol in China.

Fig. 15 shows the total flow chart of methanol in China. Most of the methanol was consumed in traditional fields, such as the formaldehyde synthesis, MTBE synthesis and acetic acid synthesis. However, the burgeoning fields such as alternative fuel (methanol fuel and DME synthesis) should not be ignored since about 33% of methanol in China consumed by the alternative fuel vehicles, the increase of China's alternative fuel vehicles industry will become a stable promotion that enhance methanol consumption in the future.

The feedstock type of methanol synthesis in China was unitary and nearly all of the methanol was produced from coal, natural gas and coke-oven gas. Due to the "deficient oil, lean gas, rich coal" energy structure in China, the feedstock type for methanol synthesis should be extended to novel materials which associated with lower cost and proper characteristics, such as coalbed methane, shale gas, etc. [77,78]. Besides that, the production of methanol derived from the synthesis of CO_2 and H_2 can be considered as an effective solution to the Greenhouse issues [79,80].

Although methanol economy is hot in China, the investment of methanol needs carefully planning, especially for west of China, where has abundant coal and natural gas but is far from the main methanol consumption region. The construction of supporting facilities (such as railway and highway) should keep pace with the building of methanol factory in order to ensure a smooth and efficient flow of methanol across China.

References

[1] Panwar NL, Kaushik SC, Kothari S. Role of renewable energy sources in environmental protection: a review. Renewable & Sustainable Energy Reviews 2011;15(3):1513–24.
[2] Kothari R, Tyagi VV, Pathak A. Waste-to-energy: a way from renewable energy sources to sustainable development. Renewable & Sustainable Energy Reviews 2010;14(9):3164–70.
[3] Ma H, Oxley L, Gibson J, Wen Li. A survey of China's renewable energy economy. Renewable & Sustainable Energy Reviews 2010;14(1):438–45.
[4] Fayaz H, Saidur R, Razali N, Anuar FS, Saleman AR, Islam MR. An overview of hydrogen as a vehicle fuel. Renewable & Sustainable Energy Reviews 2012;8 (16):5511–28.
[5] Taibi E, Gielen D, Bazilian M. The potential for renewable energy in industrial applications. Renewable & Sustainable Energy Reviews 2012;16(1):735–44.
[6] Liu YZ, Jiao WZ, Qi GS. Preparation and properties of methanol–diesel oil emulsified fuel under high-gravity environment. Renewable Energy 2011;36 (5):1463–8.
[7] Gong CM, Huang K, Jia JL, Su Y, Gao Q, Liu XJ. Improvement of fuel economy of a direct-injection spark-ignition methanol engine under light loads. Fuel 2011;90(5):1826–32.
[8] Yang CJ, Jackson RB. China's growing methanol economy and its implications for energy and the environment. Energy Policy 2012;41:878–84.
[9] Sayah AK, Sayah AK. Wind–hydrogen utilization for methanol production: an economy assessment in Iran. Renewable & Sustainable Energy Reviews 2011;15(8):3570–4.
[10] Fahy JC. The impact of Middle Eastern methanol exports to Western Europe. Energy Policy 1986;14(1):24–34.
[11] Li F. Analysis of development and trend of methanol industry in China. Coal Chemical Industry 2013;164:7–12 (in Chinese).
[12] Department of Energy Statistics. National Bureau of Statistics of China. China Energy Statistical Yearbook 2011. Beijing: 2012.
[13] An NH, Yu QS, Liu G, Li S, Jia M, Zhang WX. Complete oxidation of formaldehyde at ambient temperature over supported Pt/Fe_2O_3 catalysts prepared by colloid-deposition method. Journal of Hazardous Materials 2011;186(2):1392–7.
[14] Qian M, Liauw MA, Emig G. Formaldehyde synthesis from methanol over silver catalysts. Applied Catalysis A 2003;238(2–3):211–22.
[15] Kralj AK. Silver and oxide hybrids of catalysts during formaldehyde production. Energy 2010;35:2528–34.
[16] Sagou M, Deguchi T, Nakamura S. Dehydrogenation of methanol to formaldehyde by $ZnO–SiO_2$ and Zn_2SiO_4 catalysts. Studies in Surface Science and Catalysis 1989;44:139.
[17] Sidheswaran MA, Destaillats H, Sullivan DP, Larsen J, Fisk WJ. Quantitative room-temperature mineralization of airborne formaldehyde using manganese oxide catalysts. Applied Catalysis B 2011;107(1–2):34–41.
[18] Castillo R, Dewaele K, Ruiz P, Delmon B. Mechanical mixtures of α-Sb_2O_4 and MoO_3 as highly selective catalysts for the oxidation of methanol to formaldehyde. Applied Catalysis A 1997;153(1–2):L1–8.
[19] Prairie MR, Su S, Renzen A, Ruterana P, Buffat PA. Chemical and structural changes of Na_2MoO_4 as a methanol dehydrogenation catalyst. Applied Catalysis 1990;57(1):83–9.
[20] Wiesgickl G, Beck HP, Emig G. Novel type of catalyst for the pure dehydrogenation of methanol to formaldehyde. Applied Catalysis 1990;59(1):L1–7.
[21] Fan DB, Li JZ, Chang JM. On the structure and cure acceleration of phenol–urea–formaldehyde resins with different catalysts. European Polymer Journal 2009;45(10):2849–57.
[22] Yasuyuki M, Keiji H, Satohiro Y. Dehydrogenation of methanol to formaldehyde over silicalite. Journal of Catalysis 1986;100(2):392–400.
[23] Zhang XY, Hu HQ, Zhu YD, Zhu SW. Effect of carbon molecular sieve on phenol formaldehyde novolac resin based carbon membranes. Separation and Purification Technology 2006;52(2):261–5.
[24] Wei W, Qin GT, Hu HQ, You LB, Chen GH. Preparation of supported carbon molecular sieve membrane from novolac phenol–formaldehyde resin. Journal of Membrane Science 2007;303(1–2):80–5.
[25] Cozzolino M, Tesser R, Serio MD, Onofrio PD, Santacesaria E. Kinetics of the oxidative dehydrogenation (ODH) of methanol to formaldehyde by supported vanadium-based nanocatalysts. Catalysis Today 2007;128(3–4):191–200.
[26] Tang XJ, Bai Y, Duong A, Smith MT, Li LY, Zhang LP. Formaldehyde in China: production, consumption, exposure levels, and health effects. Environment International 2009;35(8):1210–24.
[27] Wen QB, Li C, Cai ZH, Zhang W, Gao HL, Chen LJ, et al. Study on activated carbon derived from sewage sludge for adsorption of gaseous formaldehyde. Bioresource Technology 2011;102(2):942–7.
[28] Wan YJ, Fan X, Zhu TL. Removal of low-concentration formaldehyde in air by DC corona discharge plasma. Chemical Engineering Journal 2011;171 (1):314–9.
[29] Okeke BC, Frankenberger Jr WT. Biodegradation of methyl tertiary butyl ether (MTBE) by a bacterial enrichment consortia and its monoculture isolates. Microbiological Research 2003;158(2):99–106.
[30] Li WQ, Fu F, Ma LW, Liu P, Li Z, Dai YP. A process-based model for estimating the well-to-tank cost of gasoline and diesel in China. Applied Energy 2013;102 (718):25.
[31] Yue X, Wu Y, Huang XJ, Ma Y, Pang Y, Bao XF, et al. Impact of gasoline engine deposits on light duty vehicle emissions: in-use case study in Beijing, China. Frontiers of Environmental Science & Engineering 2012;6(5):717–24.
[32] Liu HY, Yu JN, Fan Y, Shi G, Bao XJ. A scenario-based clean gasoline production strategy for China national petroleum corporation. Petroleum Science 2008;5 (3):285–94.
[33] Bielański A, Lubańska A, Poźniczek J, Micek-Ilnicka A. Oxide supports for 12-tungstosilicic acid catalysts in gas phase synthesis of MTBE. Applied Catalysis A 2003;238(2):239–50.
[34] Xia QH, Wee CH, Hidajat K, Kawi S. H3PW12O40-supported MCM-41 acid catalyst for the gas-phase synthesis of MTBE. Studies in Surface Science and Catalysis, Part C 2004;154:2915–22.
[35] Caetano NS, Loureiro JM, Rodrigues AE. MTBE synthesis catalysed by acid ion exchange resins: Kinetic studies and modeling of multiphase batch reactors. Chemical Engineering Science 1994;49(24):4589–604.
[36] Sharma MM. Some novel aspects of cationic ion-exchange resins as catalysts. Reactive and Functional Polymers 1995;26(1–3):3–23.
[37] Ali MA, Brisdon BJ, Thomas WJ. Intrinsic kinetics of MTBE synthesis from methanol and isobutene using a synthesised MFI type zeolite. Applied Catalysis A 2000;197(2):303–9.
[38] Aboul-Gheit AK, El-Awadi MY, Jehya FS. Production of environmentally friendly octane booster (methyl-t-butylether, MTBE) using zeolite catalysts. Studies in Surface Science and Catalysis 1999;125:399–407.
[39] Lu Y, Zhang L, Chen HL, Qian ZH, Gao CJ. Hybrid process of distillation side-connected with pervaporation for separation of methanol/MTBE/C4 mixture. Desalination 2002;149(1-3):81–7.
[40] Fleisch TH, Basu A, Sills RA. Introduction and advancement of a new clean global fuel: the status of DME developments in China and beyond. Journal of Natural Gas Science & Engineering 2012;9:94–107.

[41] Liu S, Cuty Clemente ER, Hu T, Wei Y. Study of spark ignition engine fueled with methanol/gasoline fuel blends. Applied Thermal Engineering 2007;27:1904–10.
[42] Carpenter AR, Hinze PC. System safety analysis of hydrogen and methanol vehicle fuels. Process Safety Programs 2004;23(4):292–9.
[43] Chang TY, Rudy SJ, Kuntasal G, Gorse RA. Impact of methanol vehicles on ozone air-quality. Atmospheric Environment 1989;23(8):1629–44.
[44] Liang B, Ge YS, Tan JW. Comparison of PM emissions from a gasoline direct injected (GDI) vehicle and a port fuel injected (PFI) vehicle measured by electrical low pressure impactor (ELPI) with two fuels: Gasoline and M15 methanol gasoline. Journal of Aerosol Science 2013;57:22–31.
[45] Wang YH, He DH, Xu BQ. Studies of producing acetic acid by carbonylation of methanol. Progress in Chemistry 2003;15(3):215–21.
[46] Hunt RW, Chinnasamy S, Das KC. The effect of naphthalene–acetic acid on biomass productivity and chlorophyll content of Green Algae, Coccolithophore, Diatom, and Cyanobacterium cultures. Applied Biochemistry and Biotechnology 2011;164(8):1350–65.
[47] Suttichai A, Jitkarun P, Piyasan P, Tomohiko T, Shigeo G. Theoretical study on the synthesis of methyl acetate from methanol and acetic acid in pervaporation membrane reactors: effect of continuous-flow modes. Chemical Engineering Journal 2003;95(1–3):57–65.
[48] Makoto Y, Kiyoshi M. Production of acetic acid from methanol by thermophilic Methanosarcina sp.: acetate production as an index in abnormal methane fermentation. Journal of Fermentation and Bioengineering 1998;86(2):239–42.
[49] Xu HY, Shi KY, Shang YC, Zhang Y, Xu GL, Wei YD. A study on the reforming of natural gas with steam, oxygen and carbon dioxide to produce syngas for methanol feedstock. Journal of Molecular Catalysis A: Chemical 1999;147(1–2):41–6.
[50] Pisarenko EV, Pisarenko VN, Minigujov RM, Abaskuliev DA. Power- and resource-saving process for producing methanol from natural gas. Theoretical Foundations of Chemical Engineering 2008;42(1):12–8.
[51] Ramos L, Zeppieri S. Feasibility study for mega plant construction of synthesis gas to produce ammonia and methanol. Fuel 2013;110:141–52.
[52] Palmer ER. Gasification of wood for methanol production. Energy in Agriculture 1984;3:363–75.
[53] Ucar MB, Ucar G. Characterization of methanol extracts from quercus hartwissiana wood and bark. Chemistry of Natural Compounds 2011;47(5):697–703.
[54] Güllü D, Demirbaş A. Biomass to methanol via pyrolysis process. Energy Conversion and Management 2001;42(11):1349–56.
[55] Chmielniak T, Sciazko M. Co-gasification of biomass and coal for methanol synthesis. Applied Energy 2003;7(3–4):393–403.
[56] Kamarudin SK, Shamsul NS, Ghani JA, Chia SK, Liew HS, Samsudin AS. Production of methanol from biomass waste via pyrolysis. Bioresource Technology 2013;129:463–8.
[57] Shen JF, Zhang ZY, Tian B, Hua YJ. Lipophilic phenols partially explain differences in the antioxidant activity of subfractions from methanol extract of camellia oil. European Food Research and Technology 2012;235(6):1071–82.
[58] Kapralova GA, Kurskii YA, Fedotov VG, Chaikin AM, Abakumov GA. A new method for producing methanol from methane. Doklady Chemistry 2006;410:178–81.
[59] Taher E, Chandran K. High-rate, high-yield production of methanol by ammonia-oxidizing bacteria. Environmental Science & Technology 2013;47(7):3167–73.
[60] Holmgren KM, Berntsson T, Andersson E, Rydberg T. System aspects of biomass gasification with methanol synthesis—process concepts and energy analysis. Energy 2012;45(1):817–28.
[61] Tatarczuk A, Zapart L, Dreszer K. Process and economic modelling of methanol production by bituminous coal gasification. Przemysł Chemiczny 2010;89(6):831–6.
[62] Wei XY, Wang XH, Zong ZM. Extraction of organonitrogen compounds from five Chinese coals with methanol. Energy & Fuels 2009;23:4848–51.
[63] Lin H, Jin HG, Gao L, Han W. Economic analysis of coal-based polygeneration system for methanol and power production. Energy 2010;35(2):858–63.
[64] Halmann M, Steinfeld A. Methanol, hydrogen, or ammonia production by tri-reforming of flue gases from coal- and gas-fired power stations. Energy-Efficient, Cost-Effective and Environmentally-Sustainable Systems and Processes 2004;1–3:1117–28.
[65] Abu Bakar S, Niwa K, Bakkerud PK. Ammonia/methanol co-production plant. Ammonia Plant Safety and Related Facilities 2000;40:292–9.
[66] Wang JL, Feng LY, Tverberg GE. An analysis of China's coal supply and its impact on China's future economic growth. Energy Policy 2013;57:542–51.
[67] Masih AM, Albinali K, DeMello L. Price dynamics of natural gas and the regional methanol markets. Energy Policy 2010;38(3):1372–8.
[68] Halmann M, Steinfeld A. Production of lime, hydrogen, and methanol by the thermo-neutral combined calcination of limestone with partial oxidation of natural gas or coal. Energy 2006;31(10–11):1533–41.
[69] Rosen MA, Scott DS. Energy and exergy analyses of a production process for methanol from natural gas. International Journal of Hydrogen Energy 1988;13(10):617–23.
[70] Birtish Pretroleum. BP statistical review of world energy; 2012. 〈http://www.bp.com/sectiongenericarticle800.do?categoryId=9037178&contentId=7068624〉.
[71] Zhang JY, Zhang XH, Chen Z, Li L. Thermodynamic and kinetic model of reforming coke-oven gas with steam. Energy 2010;35(7):3103–8.
[72] Bermúdez JM, Arenillas A, Menéndez JA. Equilibrium prediction of CO_2 reforming of coke oven gas: suitability for methanol production. Chemical Engineering Science 2012;82:95–103.
[73] Bermúdez JM, Fidalgo B, Arenillas A, Menéndez JA. CO_2 reforming of coke oven gas over a Ni/γ Al_2O_3 catalyst to produce syngas for methanol synthesis. Fuel 2012;94:197–203.
[74] Bermúdez JM, Fidalgo B, Arenillas A, Menéndez JA. Dry reforming of coke oven gases over activated carbon to produce syngas for methanol synthesis. Fuel 2010;89(10):2897–902.
[75] Lange JP. Methanol synthesis: a short review of technology improvements. Catalysis Today 2001;64(1–2):3–8.
[76] Guo DG, Zhang XY, Shao HB, Bai ZK, Chu LY, Shangguan TL, et al. Energy plants in the coastal zone of China: category, distribution and development. Renewable & Sustainable Energy Reviews 2011;15(4):2014–20.
[77] Xu F, Zhu LH. Synthesis of methanol from oxygen-containing coalbed methane and environmental benefit analysis. Disaster Advances 2010;3(4):407–10.
[78] Armor JN. Emerging importance of shale gas to both the energy & chemicals landscape. Journal of Energy Chemistry 2013;22(1):21–6.
[79] Tidona B, Koppold C, Bansode A, Urakawa A, von Pohra PR. CO_2 hydrogenation to methanol at pressures up to 950 bar. Journal of Supercritical Fluids 2013;78:70–7.
[80] Boretti A. Renewable hydrogen to recycle CO_2 to methanol. International Journal of Hydrogen Energy 2013;38(4):1806–12.